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(54) Degradable aliphatic polyester formed products

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Descripti n**Background of th nvention**5 **1. Field of the Invention**

[0001] The present invention relates to a degradable aliphatic polyester formed product that can be degraded after use in the natural environment with ease.

10 **2. Description of the Related Art**

[0002] Conventionally, formed product such as foams, fabrics for industrial materials, filaments, decomposable non-woven fabrics, composite materials and films have been prepared from polyolefin, polyurethane, polyamide and other resins. These formed products, however, have a very slow rate of decomposition in the natural environment and semipermanently remain under the ground when buried in disposal. Further, abandoned plastics lead to problems by impairing the view or destroying the living environment of marine organisms. When the refuse is disposed by incineration, toxic gases develop and cause destruction of environment on earth and additionally lead to problems by accelerating deterioration of incinerators.

[0003] Foams have been widely applied to thermal insulation materials and shock absorbers. These foams can be prepared from a small amount of resin and thus are utilized for light weight and cheap containers of food, thermal insulation materials and shock absorbers. However, forms prepared from these resins are bulky and increase amount of refuse when they are abandoned after use.

[0004] Conventional fabrics also cause similar problems, though excellent as an industrial material.

[0005] As to bioabsorbable surgical filaments, conventionally, mainstream catgut were prepared by dividing and purifying small intestine tissue of a cow and successively polishing into the form of fishing strings have drawbacks of rapid decrease of the tensile strength retention in a body and also of great difference depending upon a patient in the rate of absorption into the body. Thus, conventional catguts are being replaced by synthetic filaments.

[0006] A silk thread hydrolyzes after the lapse of a long period in a living body and is used for a suture portion which requires decomposition in a living body, for example, in the case of suture of intestines. A silk thread, however, is deficient in strength and thus synthetic filaments are also replacing a silk thread.

[0007] Synthetic filaments prepared from polyglycolic acid are most frequently used for absorbable surgical sutures, and Opeporix, Dexon and Medifit in which polyglycolic acid is used as a base material are put on the market. However, polyglycolic acid sutures are applied in the form of a multifilament because polyglycolic acid homopolymer has high stiffness. Polyglactin 910® (product of Ethicon Co.) is a copolymer of glycolide and lactide and put on the market also in the form of a multifilament due to the same reason.

[0008] On the other hand, a suture based on a copolymer of polydioxanone and glycolide is characterized by softness and a slow rate of decomposition in a living body. Additionally, the suture is elastic and is put on the market in the form of a monofilament. However, any synthetic filaments mentioned above have problems of very high prices.

[0009] As to fishing lines, synthetic filaments of polyamide such as nylon 6 and of polyester such as polyethylene terephthalate are now used. These fishing lines require high strength and long life and thus synthetic filaments having such characteristics have been developed. For example, polyamide or aromatic polyester filaments have been disclosed in Japanese Laid-Open Patent SHO 63-227812 and 63-317032, respectively. Consequently, any of these fishing lines can semipermanently maintain high strength even in water so that polymers or metals which are quite or almost non degradable in water have been used for the raw material.

[0010] In recent years, however, fishing tackle which was abandoned or left to stand in the sea, rivers, lakes and marshes has led to problems for the harmful effect on nature such as impairment of natural environment and injury to birds and aquatic organisms. For example, fishing lines and fitted fishhooks which were abandoned or left to stand in water due to some reasons such as catch on a rock or stake have been known to cause trouble on the navigation of ships by wrapping themselves around a screw of the ship or to give considerably adverse effect on the ecological system by coiling around birds and aquatic organisms. These subjects have become a serious social problem with increase in the fishing population.

[0011] The term "nonwoven fabrics" means a cloth like matter prepared without weaving or knitting, and more particularly means a cloth like matter obtained by bonding or intertwining combining constitutional filaments of a web composed of fibrous substance without applying weaving or knitting. Conventionally, nonwoven fabrics have been widely used for center layers of garment, carpets, diapers, sanitary articles and industrial materials. Fibrous materials which constitute nonwoven fabrics are polyolefines such as polypropylene, aromatic polyesters such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyamides such as nylon and cellulose such as rayon. Nonwoven fabrics prepared from these polymers and preparation processes thereof have been disclosed, for example, in

Japanese Laid-Open Patent SHO 59-88961, 59-94658 and 59-94660.

[0012] Conventional packaging containers are prepared by using a composite material composed of a polyolefine resin such as polyethylene or polypropylene and a paper or a regenerated cellulose film (cellophane), and widely used for water-resistant packaging containers for packing milk and juice. Coated papers having a smooth and glossed surface are frequently used for book covers and toiletry boxes in order to satisfy aesthetic desire of consumers. However, in the case of recycling paper as pulp resources, films inhibit a disaggregation step of pulp and decrease efficiency. Further, splinters of the polymer are liable to contaminate recovered pulp and thus a technique for isolating the polymer from macerated pulp is also needed.

[0013] Japanese Laid-Open Patent HEI 4-336246 has disclosed a laminated material prepared from polylactic acid and paper and degradable under natural environment. Japanese Laid-Open Patent HEI 4-38784 has also disclosed a composite film of polylactic acid and a regenerated cellulose film. Polylactic acid, however, is a rigid polymer having low elongation and thus paper or a regenerated cellulose film laminated with the polymer is liable to develop cracks due to breakage of the polymer film in the case folding the laminate. Barrier properties against liquid, gas and micro-organisms are important in order to use such a composite film as a container for preserving milk, juice and cakes. Generation of cracks by folding is unfavorable.

[0014] Films prepared from conventional polymers are excellent packaging materials. These films, however, lead to the above various problems.

[0015] An aliphatic polyester had been known as a thermoplastic and degradable polymer. The esterification reaction of polyhydric alcohol and polybasic acid is a successive reaction and a molecular weight of the formed polymer increases with reaction time. However, water generated in the reaction reduces the molecular weight of polycondensate by hydrolysis. Consequently, it has been thought that an aliphatic polyester obtained by direct polycondensation has a maximum molecular weight of about 10,000.

[0016] Japanese Laid-Open Patent HEI 4-189822, 4-189823, 5-105736, 5-140284, 5-140285, 5-140286, 5-140287 and 5-140288 have described a preparation process of a high molecular weight polyester by adding diisocyanate at a NCO/OH equivalent ratio of 1/10 - 2 to saturated polyester wherein a number average molecular weight is 5,000 or more. terminal groups are substantially hydroxyl and the acid component is a compound having 3 and more carbon atoms or a mixture thereof, in a molten state above the melting point of said saturated polyester. However, isocyanate used as a raw material of high polymers generates strongly toxic diamine in the course of polymer degradation, and the diamine accumulates under the ground. When such polymer is used for a packaging material of foodstuffs, diamine generated by decomposition is liable to contaminate the content.

[0017] Japanese Laid-Open Patent HEI 5-310898 has disclosed a preparation process of a high molecular weight aliphatic polyester comprising conducting esterification of a glycol component with an aliphatic or alicyclic dicarboxylic acid component or an acid anhydride component thereof and subjecting the resultant polyesterdiol to deglycolation at 180 -230 °C under high vacuum of 0.005-0.1 mm Hg in the presence of a catalyst.

[0018] USP 3,850,862 and 3,932,319 have described a preparation process of aliphatic polyester having an reduced viscosity of 0.1- 10 by polymerizing at 250 °C or more under high vacuum of 1 mm Hg or less and successively conducting an ester exchange reaction under extra-high vacuum of 10^{-3} mm Hg or less, and a novel mixture obtained by adding a natural biodegradation product to said aliphatic polyester. However, the synthetic process of aliphatic polyester by reacting at such a high temperature inevitably leads to generation of impurities and resultant coloration.

[0019] An aliphatic polyester undergoes hydrolysis with relative ease in the presence of water and can also be decomposed by microorganisms, and thus can be applied to the above uses. However, foams, fabrics, filaments, composites with cellulose and films have not yet been known concerning the aliphatic polyester.

[0020] EP-A-0 618 249 is prior art under the provisions of Art. 54(3) and (4) EPC and discloses a method for preparing an aliphatic polyester having high molecular weight. This aliphatic polyester can be used in the form of films, filaments, shaped articles, foams and nets.

Summary of the Invention

[0021] The object of the invention is to provide a formed product of a thermoplastic degradable polymer which is prepared by a direct condensation of a polyhydric alcohol and a polybasic acid or additionally a hydroxycarboxylic acid and can be decomposed with ease in the natural environment so as to overcome defects of conventional technology.

[0022] As a result of an intensive investigation in order to solve the above problems, the present inventors have found that a formed product of an aliphatic polyester resin can be obtained by using a high molecular weight aliphatic polyester which is prepared by a direct polycondensation reaction of an aliphatic polyhydric alcohol or a mixture thereof with an aliphatic polybasic acid or a mixture thereof or additionally an aliphatic hydroxycarboxylic acid or a mixture thereof, or on oligomer thereof, in a reaction mixture including an organic solvent. Thus the present invention has been completed.

[0023] That is, the aspect of the invention is a degradable thermoplastic polymer formed product, i.e. a fabric or a

nonwoven fabric, comprising an aliphatic polyester having a molecular weight of 50,000 or more which is obtained by conducting a direct polycondensation reaction of an aliphatic polyhydric alcohol or a mixture thereof with an aliphatic polybasic acid or a mixture thereof, or additionally a hydroxycarboxylic acid or a mixture thereof, or an oligomer resulting from these raw materials, in a reaction mixture comprising an organic solvent, with the proviso that the fabric is no net.

[0024] The fabric obtained in the invention can be used for an industrial material.

[0025] The nonwoven fabric of the invention is prepared by bonding or intertwining a web of the filament.

[0026] The resin formed product of the invention including a fabric for an industrial material and a degradable nonwoven fabric, can be degraded similarly to paper, wood and other natural products into nontoxic water and carbon dioxide within a certain period in the natural environment.

Detailed Description of Preferred Embodiments

[0027] Aliphatic polyester used in the invention is prepared by esterification of an aliphatic polyhydric alcohol or a mixture thereof with an aliphatic polybasic acid or a mixture thereof. These monomers can also include a hydroxycarboxylic acid or a mixture thereof, or an oligomer or these raw materials. Aliphatic polyester can be obtained by conducting a direct polycondensation reaction in a reaction mixture containing an organic solvent.

[0028] Polymerization degree of aliphatic polyester is 100 - 20,000. Polymerization degree lower than 100 results in a low strength of formed products and is not adapted to practical use. On the other hand, when the polymerization degree is too high, melt viscosity rises up and reduces melt processing ability.

[0029] The direct polycondensation reaction is carried out in an organic solvent by heating a mixture of a polyhydric alcohol and a polybasic acid or additionally a hydroxycarboxylic acid, while distilling out generated water and excess monomer together with the organic solvent from the reaction system and charging to the reaction system an additional organic solvent containing an amount of water and monomer not more than that dissolved in the distilled organic solvent.

[0030] Polyhydric alcohols of the invention have aliphatic hydroxyl groups and include, for example, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, neopentyl glycol, polytetramethylene glycol, 1,4-cyclohexanedimethanol and 1,4-benzenedimethanol.

[0031] Exemplary polybasic acids of the invention have aliphatic carboxyl groups and include succinic acid, oxalic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecane diacid, dodecane diacid, 1,4-phenylenediacetic acid and phenylsuccinic acid. Anhydrides of these polybasic acids can also be used.

[0032] Representative hydroxycarboxylic acids which can be used include lactic acid, glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 3-hydroxyvaleric acid, 5-hydroxyvaleric acid and 6-hydroxycaproic acid. When these raw materials have an asymmetric carbon atoms in the molecule, individual D-, L-, DL-isomer and a mixture thereof can be used.

[0033] In order to obtain a nonwoven fabric having a smooth surface, polymer is preferably prepared in view of economy from ethylene glycol as a polyhydric alcohol and succinic acid as a polybasic acid.

[0034] When lactic acid or glycolic acid is added as a hydroxycarboxylic acid, the proportion is preferably 50 % or less, more preferably 20 % or less.

[0035] The polycondensation reaction can progress by heating in the absence of a catalyst. The catalyst, however, can accelerate a reaction velocity. The catalysts which can be used in the invention are metals of the group II, III, IV, and V in the periodic table and oxides or salts thereof. Exemplary catalysts include zinc powder, tin powder, aluminum, magnesium, titanium, germanium and other metals; tin oxide, antimony oxide, zinc oxide, aluminum oxide, magnesium oxide, titanium oxide and other metal oxides; stannous chloride, stannic chloride, stannous bromide, stannic bromide, antimony fluoride, zinc chloride, magnesium chloride, aluminum chloride and other metal halogenides; tin sulfate, zinc sulfate, aluminum sulfate and other metal sulfates; magnesium carbonate, zinc carbonate and other metal carbonates; tin acetate, stannous octoate, tin lactate, zinc acetate, aluminium acetate and other metal organic carboxylates; tin trifluoromethanesulfonate, zinc trifluoromethanesulfonate, magnesium trifluoromethanesulfonate, tin methanesulfonate, tin p-toluenesulfonate and other metal organic sulfonates; dibutyltin oxide and other organic metal oxides of the above metals; titanium isopropoxide and other metal alkoxide of the above metals; diethyl zinc and other alkyl metal of the above metal; and DOWEX®, AMBERLITE® and other ion exchange resins.

[0036] The amount in use of these catalysts is usually 0.0001 - 10 wt%, preferably 0.001 - 2 wt% in view of economy for the total amount of aliphatic polyhydric alcohol and aliphatic polybasic acid or aliphatic polyhydric alcohol, aliphatic polybasic acid and aliphatic hydroxycarboxylic acid to be used, or an oligomer of these raw materials.

[0037] Exemplary solvents which can be used for preparing aliphatic polyester of the invention include, for example, toluene, xylene, mesitylene and other hydrocarbon solvents; chlorobenzene, bromobenzene, iodobenzene, dichlorobenzene, 1,1,2,2-tetrachloroethane, p-chlorotoluene and other halogenated hydrocarbon solvents; 3-hexanone, acetophenone, benzophenone and other ketone solvents; dibutyl ether, anisole, phenetol, o-dimethoxybenzene, p-

dimethoxybenzene, 3-methoxytoluene, dibenzyl ether, benzyl phenyl ether, methoxynaphthalene and other ether solvents; diphenyl sulfide, thioanisole and other thioether solvents; methyl benzoate, dimethyl phthalate, diethyl phthalate and other ester solvents; diphenyl ether, 4-methyldiphenyl ether, bis(3-methylphenyl)ether, 3-phenoxy toluene and other alkyl substituted diphenyl ether solvents; 4-bromodiphenyl ether, 4-chlorodiphenyl ether, 4-methyl-4'-bromodiphenyl ether and other halogen substituted diphenyl ether solvents; 4-methoxydiphenyl ether, 4-ethoxydiphenyl ether, 3-methoxydiphenyl ether, 4-methyl-4'-methoxydiphenyl ether and other alkoxy substituted diphenyl ether solvents; and dibenzofuran, xanthene and other cyclic diphenyl ether solvents. These solvents can be used singly or as a mixture. Solvents which can be separated from water with ease is preferable. In order to obtain polyester having a high average molecular weight in particular, ether solvents, alkyl aryl ether solvents and diphenyl ether solvents are more preferably used, and alkyl aryl ether solvents and diphenyl ether solvents are most preferably used.

[0038] These solvents are preferably used in an amount so as to obtain a polymer concentration of 10 - 80 %.

[0039] In the preparation of aliphatic polyester, generated water and excess monomer are preferably distilled out of the reaction system by azeotropic distillation of the organic solvent and water or the monomer.

[0040] When an azeotropically distilled solvent contains water or the monomer in an amount higher than the solubility of water or the monomer in said organic solvent, water or the monomer is removed by separation and a residual organic solvent can be successively returned to the reaction system. In order to further remove water and a monomer which are still dissolved in the organic solvent after separation, the organic solvent can be dehydrated, treated with a monomer removing agent or redistilled, and a solvent containing a reduced amount of water and monomer can be returned to the reaction system.

[0041] Alternatively, a new organic solvent having a low content of water and monomer can be charged in place of the azeotropically distilled organic solvent.

[0042] Further, water and excess monomer can be removed under reduced pressure in the first stage of the reaction, an organic solvent is successively added and a portion of the organic solvent can be removed from the reaction mixture to adjust content of water and monomer to a prescribed value in the reaction mixture. That is, the polycondensation reaction proceeds while removing water and the excess monomer with the aid of a solvent at least at a certain stage of the reaction. In an embodiment of the reaction, solvent can or cannot be azeotropically distilled with or separated from water and monomer.

[0043] Other embodiments which can be included are a process for previously charging a solvent in excess and carrying out dehydration and monomer removal merely by removing the solvent, a process for carrying out dehydration and monomer removal of the solvent by using a different kind of solvent, and a modified process for removing water and monomer in the liquid state of reaction solvent itself. As to reaction temperature, the reaction can be carried out at the azeotropic temperature of the solvent with water and monomer. In the case the dehydration reaction comes nearly to the end, the boiling point of the solvent system may increase. However, there is no problem in the case if the reaction is conducted in a given temperature range.

[0044] The average molecular weight (a weight average molecular weight unless otherwise specified) of the aliphatic polyester depends also upon the content of water and monomer in the organic solvent charged to the reaction system, although it depends on the kind of solvent. When the solvent has a high water and monomer content of 400-500 ppm, aliphatic polyester obtained has a weight average molecular weight of 15,000 - 50,000. It is surprising that, even under the high water and monomer content as above, aliphatic polyester having a weight average molecular weight of 40,000-50,000 can be obtained by using a diphenyl ether base solvent. In order to further increase the average molecular weight of aliphatic polyester, it is desired to reduce the water and monomer content of the organic solvent charged to the reaction system. Accordingly, azeotropically distilled organic solvent is dehydrated or treated with a dehydrating agent to reduce or remove water and monomer and thereafter returned to the reaction system. Alternatively, a new organic solvent having a low content of water and monomer is charged to the reactor. These procedures can reduce the amount of water and monomer to 50 ppm or less, and provide an aliphatic polyester having a weight average molecular weight of 50,000 - 300,000.

[0045] Exemplary dehydrating and monomer-removing agents which can be used for preparing the high molecular weight polyester for use in the nonwoven fabric of the invention include molecular sieve 3A, molecular sieve 4A, molecular sieve 5A, molecular sieve 13X and other molecular sieves; alumina, silica gel, calcium chloride, calcium sulphate, diphosphorus pentoxide, concentrated sulphuric acid, magnesium perchlorate, barium oxide, calcium oxide, potassium hydroxide, sodium hydroxide; calcium hydride, sodium hydride, lithium aluminum hydride and other metal hydrides; and sodium and other alkali metals. Molecular sieves are preferred in these agents in view of ease for handling and recovery.

[0046] An exemplary preparation process of polyester in the invention will be illustrated below.

[0047] That is, a solvent, a prescribed amount of ethylene glycol, succinic acid and lactic acid, and a prescribed amount of a catalyst are charged to a reaction vessel equipped with a separator, for example, a Dean Stark Trap. The reaction vessel is heated and azeotropically distilled solvent, water and excess monomer are introduced into the separator. Water and monomer which exceed solubility in the solvent are separated in the separator and removed from the

reaction system. The residual solvent saturated with water and monomer is returned to the reaction system. The weight average molecular weight of the polymer is 500 - 1,000 in this stage and can be increased to 5,000. The reaction time is from 0.5 to several hours. The oligomerization reaction can be previously carried out in a separate reaction vessel under a reduced pressure in the absence of a solvent and catalyst, or in a solvent in the absence of a catalyst.

[0048] The reaction can be continued at the azeotropic distillation temperature of the solvent while removing generated water and excess monomer with the progress of the reaction and returning the solvent saturated with water and monomer to the reaction system. Such a process, however, merely provides a polymer having an average molecular weight of 15,000 - 50,000 depending upon the solvent even after reacting for dozens of hours.

[0049] In order to obtain a polymer having a higher molecular weight, the separator is dismantled after distilling most of excess monomer and water contained in the raw materials and a tube packed with a drying agent such as molecular sieves is mounted on the reaction vessel so as to return the distilled solvent to the reaction vessel by way of the tube. Alternatively, the distilled solvent may come into contact with a drying agent in another reaction vessel and successively returns to the reaction system, or a new solvent having a low content of water and monomer may be fed to the reaction vessel. The amount of water and monomer dissolved in the solvent is reduced to 50 ppm or less by such configuration of equipment. When the reaction is continued for dozens of hours under these conditions, a polymer having a weight average molecular weight of 50,000 - 300,000 can be obtained depending upon the solvent. After finishing the reaction, the polymer can be isolated by any methods. For example, the reaction mixture is dissolved in chloroform by heating, cooled and poured into acetone. The precipitated crystals are filtered and dried to obtain the desired polymer.

[0050] The weight average molecular weight of aliphatic polyester obtained by the process varies depending upon kind of the solvent, kind and amount of the catalyst, reaction rate, reaction time and treating method of the azeotropically distilled solvent and is usually in the range of 15,000 - 300,000. In the case of carrying out polycondensation reaction of the invention in the presence of a catalyst, a residual catalyst in the polymer obtained gives adverse effect on the thermal stability and weatherability. Accordingly, it is preferred to remove the residual catalyst in the polymer. A preferred removing method is to cool the reaction mixture with stirring or as intact and to bring the resulting powdery or solid polymer into contact with an acidic substance in the presence of a hydrophilic organic solvent.

[0051] Hydrophilic organic solvents which can be used for the method include, for example, methanol, ethanol, isopropanol, butanol and other alcohols; acetone, methyl ethyl ketone and other ketones; tetrahydrofuran, dioxane and other ethers; acetic acid, butyric acid and other carboxylic acids; acetonitrile and other nitriles; and N,N-dimethylformamide, N,N-dimethylacetamide, 1,3-dimethylimidazolidinone, hexamethylphosphoramide and other amides. Preferred organic solvents are alcohols which are cheap and do not dissolve the polymer.

[0052] Exemplary acidic substances include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and other inorganic acids; and acetic acid, p-toluenesulfonic acid and other organic acids. Hydrochloric acid, sulfuric acid and nitric acid are particularly preferred because of cheapness.

[0053] The amount of the acidic substance is usually 0.0001-5.0 mols, preferably 0.001 - 1 mol for 100 parts by weight of the polymer. When the amount is less than 0.0001 mol, removing effect on the catalyst is reduced. On the other hand, the amount larger than 5.0 mols is liable to cause problems on deterioration.

[0054] Morphology of a solid polymer used in the method is powder, granule, particle, flake and block. The polymer is generally obtained by dissolving the polymer in a good solvent and dropwise adding the solution to a lean solvent or vice versa, or by thermally dissolving the polymer in a specific solvent and successively cooling the solution to cause crystallization of the polymer.

[0055] Bulk density of the polymer is preferably 0.60 g/ml or less, more preferably 0.05 - 0.5 g/ml. Bulk density higher than 0.60 g/ml leads to insufficient contact with the acidic substance and the catalyst in the polymer cannot be completely removed in some cases. On the other hand, bulk density lower than 0.05 g/ml causes no problem on the catalyst removal, but impairs filterability after treatment and sometimes results in problems on operation.

[0056] Polymer is brought into contact with an acidic substance under conditions such as a solid concentration of preferably 3 - 40 % by weight in a hydrophilic organic solvent, a contact temperature of preferably 0 - 100 °C, more preferably 0 - 60 °C, and a contact time of preferably 0.1 - 24 hours, more preferably 0.5 - 8 hours.

[0057] Aliphatic polyester of the invention is converted to a thermoplastic polymer composition by formulating with a usually known thermoplastic polymer, plasticizer and various kind of additives and modifiers. The additives and modifiers which can be used, when necessary, are a plasticizer, ultraviolet absorber, light stabilizer, heat stabilizer, lubricant, antioxidant, colorant, flame retardant, filler and so on.

[0058] The proportion of aliphatic polyester in the thermoplastic polymer composition varies depending upon desired degradability and a proportion of 50 % or more is generally preferred. Any known kneading technique is applicable to the preparation of thermoplastic polymer composition.

[0059] The thermoplastic polymer composition thus obtained can be used in the form of pellet, rod or powder.

[0060] The present inventors have further found that the above aliphatic polyester can provide a fabric having excellent properties such as thermal insulation, strength and elongation, and that the fabric can be used for an industrial material without impairing degradability of the polymer. In order to obtain a fabric from the thermoplastic polymer com-

position of the invention, the composition is generally processed into a filament by melt-spinning process and successively processed into a fabric with an weaving machine.

[0061] No particular restriction is imposed upon the melt-spinning equipment for use in filament preparation so long as the equipment is fitted with a melting zone comprised of a cylinder and screw which have a temperature control unit, and a spinning head part fitted with a spinning nozzle. Spinning temperature depends upon kind and molecular weight of the polymer and is generally in the range of 80 - 300 °C, preferably 100 - 250 °C. The temperature lower than 80 °C leads to high melt viscosity and a filament having good properties cannot be obtained. The temperature higher than 300 °C unfavorably causes decomposition.

[0062] Commonly used spinning nozzles can be used for preparing the monofilament in the invention. For example, a preferred nozzle has a bore diameter of 0.3 mm or less. A molten monofilament delivered is cooled, stretched in a hot heat-medium and successively heat-set to obtain a filament. Stretching conditions such as a stretching temperature and a stretch ratio are suitably selected depending upon the properties required for the filament and usually above the glass transition temperature and below the melting point. For example, the filament is preferably stretched in a temperature range of 0 - 100 °C at a stretch ratio of 4 - 15. It is also desired to perform stretching in a multi stage of two step or more.

[0063] Size of the filament is preferably 100 - 1300 deniers in order to obtain a fabric useful for industrial materials. The filament obtained is generally woven into a fabric with a common weaving for use in synthetic fiber, for example, a heavy cloth weaving machine for preparing canvas and concrete-curing sheet.

[0064] The fabric thus obtained is applied to industrial materials corresponding to desired uses. A preferred fabric of the invention which is useful for industrial materials has a plain-weaved structure wherein the filaments in the longitudinal and transverse directions are alternately woven, and also has a filament size of 100 - 1300 deniers and a void volume in the fabric of 50 - 74 %. When the void volume is less than 50 %, amount of resin penetration into the void of the fabric is too small in the case of laminating the fabric with resin and adhesion strength becomes insufficient. On the other hand, a void volume of greater than 74 % leads to low fabric strength and is unsuitable for industrial materials.

[0065] Thus obtained fabric of the thermoplastic polymer composition comprising an aliphatic polyester has high flexibility as compared to a fabric of conventionally known biodegradable polyhydroxycarboxylic acid.

[0066] For example, as clearly seen in the examples below, the fabric of the invention has a tensile elastic modulus which is a fraction or less as compared with a polylactic acid fabric, exhibits satisfactory softness, has similar properties to polyethylene fabric and can be suitably used for flexible industrial materials.

[0067] The present inventors have still further found that a nonwoven fabric having excellent properties such as strength and feeling can be obtained by bonding a web comprised of a filament having the above aliphatic polyester, and that the nonwoven fabric can be prepared without impairing the degradability of the polymer. That is, a degradable nonwoven fabric can be obtained by bonding a web comprised of a filament having aliphatic polyester.

[0068] The nonwoven fabric of the invention can be prepared by spinning aliphatic polyester, successively forming a web, and bonding the web by conventionally known methods, for example, a needle-punching method, stitch bonding method, jet bonding method, thermal bonding method and resin bonding method.

[0069] Known spinning processes can be applied to spin the raw material filament. Applied processes are, for example, a melt spinning process for carrying out melt spinning with an extruder, a wet spinning process for dissolving the resin comprising the above aliphatic polyester and delivering the resin solution from a nozzle to a lean solvent and a dry spinning process for delivering the resin solution from the nozzle to dry gas. Melt spinning process can be carried out with a known extruder such as a singly screw extruder and twin screw extruder. Low extrusion temperature is difficult to provide extrusion stability and is liable to cause overload. On the other hand, when the extrusion temperature is too high, heat decomposition of the polymer is accelerated and leads to lowering of molecular weight, decrease in strength and color development. In view of these problems, extrusion temperature is in the range of preferably 80 - 300 °C, more preferably 100 - 250 °C.

[0070] Bore diameter of the extrusion nozzle is suitable determined in relation to the required diameter (size) of the filament, delivery rate of the extruder and take-up speed. Preferred diameter is 0.1 - 3.0 mm.

[0071] Stretching of a spun filament is not always required in any spinning method. In the case of stretching the filament, the stretch ratio is usually 1.1 - 10, preferably 2 - 8. Stretching temperature is in the range of 0 - 100 °C.

[0072] Preferred size of the filament is 0.5 - 40 deniers. Preferred length of the filament is 0.5-30 cm.

[0073] A massed state of filaments called a web is formed from the filament obtained. The filament is not bonded each other in the state of the web. Consequently, the web cannot be called as intact as a nonwoven fabric.

[0074] Known processes are used for preparation of the web and not restricted in particular. Exemplary processes include, for example, a card process using a flat card machine, roller card machine and garnet, and a melt-blown process. Another process which can also be used is a spun bonding process for blowing high speed air to the outlet of a spinning nozzle in the spinning of the resin and forming a web by collecting delivered filaments on a perforated conveyor situated perpendicularly to the direction of air flow.

[0075] The degradable nonwoven fabric of the invention can be prepared by using known processes from a web comprised of filaments of resin consisting essentially of the above aliphatic polyester. Known processes include for example, a needle punching process using a needle, stitch bonding process using a thread, jet bonding process using water jet, thermal bonding process using heat adhesion and resin bonding process using resin adhesion.

[0076] The filament consisting essentially of aliphatic polyester of the invention can comprise, when necessary, a plasticizer, ultraviolet absorber, light stabilizer, heat stabilizer, lubricant, antioxidant and other additives.

[0077] The thus obtained nonwoven fabric of the thermoplastic polymer composition comprising an aliphatic polyester has excellent known nonwoven fabric of biodegradable polyhydroxycarboxylic acid. For example, as clearly seen in the examples below, the nonwoven fabric of the invention has a higher impact resilience than conventional nonwoven fabric of polylactic acid, also has a good feeling, and exhibits similar properties to nonwoven fabric of polyethylene. Consequently, nonwoven fabric of the invention can be suitably applied to uses which require elasticity and smoothness, for example, diapers, sanitary goods and other industrial materials.

EXAMPLE

[0078] The present invention will now be illustrated in detail by way of examples and comparative examples.

[0079] The weight average molecular weight in the examples was measured by gel permeation chromatography at a column temperature of 40 °C in a chloroform solvent using polystyrene as a reference sample.

Preparation Example 1

[0080] To 20.0 g of ethylene glycol and 38.1 g of succinic acid, 207.0 g of diphenyl ether and 0.931 g of metallic tin were added and the mixture was oligomerized by heating at 130 °C for 7 hours with stirring under reduced pressure of 140 mm Hg while distilling water out of the reaction system. Successively, a Dean Stark Trap was mounted on the reaction vessel and azeotropic dehydration was carried out at 140 °C for 8 hours under reduced pressure of 30 mm Hg. Thereafter a tube packed with 20 g of molecular sieve 3A was fitted on the reaction vessel so as to return the distilled solvent to the reaction vessel after passing through the molecular sieve layer and the reaction mixture was stirred at 130 °C for 49 hours under reduced pressure of 17 mm Hg.

[0081] The reaction mass obtained was dissolved in 400 ml of chloroform, reprecipitated by pouring the resulting solution into 3 ℓ of acetone, sludged 3 times for each 0.5 hour with an isopropyl alcohol (hereinafter referred to as IPA) solution containing 0.7 wt% of HCl, washed with IPA and dried at 60 °C for 6 hours under reduced pressure.

[0082] Polymer thus prepared had a weight average molecular weight of 124,000 and a residual tin catalyst content of 10 ppm or less.

Preparation Example 2

[0083] To 50.5 g of 1,4-butanediol and 66.5 g of succinic acid, 293.0 g of diphenyl ether and 2.02 g of metallic tin were added and an oligomer was prepared by heating the mixture at 130 °C for 7 hours with stirring under reduced pressure of 140 mm Hg while distilling water out of the reaction system. Successively, a Dean Stark Trap was mounted on the reaction vessel and azeotropic dehydration was carried out at 140 °C for 8 hours under reduced pressure of 30 mm Hg. Thereafter a tube packed with 40 g of molecular sieve 3A was fitted on the reaction vessel so as to return the distilled solvent to the reaction vessel after passing through the molecular sieve layer and the reaction mixture was stirred at 130 °C for 49 hours under reduced pressure of 17 mm Hg.

[0084] The reaction mass obtained was dissolved in 600 ml of chloroform, reprecipitated by pouring the resulting solution into 4ℓ of acetone, sludged 3 times for each 0.5 hour with an IPA solution containing 0.7 wt% of HCl, washed with IPA and dried at 60 °C for 6 hours under reduced pressure. Polymer thus prepared had a weight average molecular weight of 118,000 and a residual tin catalyst content of 10 ppm or less.

Preparation Example 3

[0085] To 80.8 g trans-1,4-cyclohexanedimethanol and 66.5 g of succinic acid, 293.0 g of diphenyl ether and 2.02 g of metallic tin were added and the mixture was oligomerized by heating at 130 °C for 7 hours with stirring under reduced pressure of 140 mm Hg while distilling water out of the reaction system. Successively, a Dean Stark Trap was mounted on the reaction vessel and azeotropic dehydration was carried out at 140 °C for 8 hours under reduced pressure of 30 mm Hg. Thereafter a tube packed with 40 g of molecular sieve 3A was fitted on the reaction vessel so as to return the distilled solvent to the reaction vessel after passing through the molecular sieve layer and the reaction mixture was stirred at 130 °C for 40 hours under reduced pressure of 17 mm Hg.

[0086] The reaction mass obtained was dissolved in 600 ml of chloroform, reprecipitated by pouring the resulting

solution into 4 ℓ of acetone, sludged 3 times for each 0.5 hour with an IPA solution containing 0.7 wt% of HCl, washed with IPA and dried at 60°C for 6 hours under reduced pressure. Polymer thus prepared had a weight average molecular weight of 122,000 and a residual tin catalyst content of 10 ppm or less.

5 Preparation Example 4

[0087] To 20.2 g of ethylene glycol, 38.5 g succinic acid and 7.3 g of lactic acid, 123.0 g of diphenyl ether and 0.66 g of metallic tin were added, and the mixture was oligomerized by heating at 125 °C for 9 hours with stirring under reduced pressure of 140 mmHg while distilling water out of the reaction system. Successively, a Dean Stark Trap was mounted on the reaction vessel and azeotropic dehydration was carried out at 140°C for 3 hours under reduced pressure of 15 mmHg. Thereafter a tube packed with 30 g of molecular sieve 3A was fitted on the reaction vessel so as to return the distilled solvent to the reaction vessel after passing through the molecular sieve layer and the reaction mixture was stirred at 130 °C for 33 hours under reduced pressure of 13 mm Hg.

[0088] The reaction mass obtained was dissolved in 720 ml of acetonitrile. The resulting solution was mixed with 300 ml of a 1N aqueous HCl solution, stirred for 0.5 hour, mixed with 320 ml of IPA and successively reprecipitated by pouring the mixture into 4.5 ℓ of methanol. The precipitate was washed with 3 ℓ of n-hexane and dried under reduced pressure. Polymer thus obtained had a weight average molecular weight of 147,000 and a residual tin catalyst content of 10 ppm or less.

20 Preparation Example 5

[0089] To 35.0 g of 1,4-butanediol, 30.4 g of succinic acid and 9.4 g of adipic acid, 176 g of diphenyl ether and 0.66 g of metallic tin were added and the mixture was oligomerized by heating the mixture at 130 °C for 10 hours with stirring under reduced pressure of 140 mm Hg while distilling water out of the reaction system. Successively, a Dean Stark Trap was mounted on the reaction vessel and azeotropic dehydration was carried out at 140 °C for 5 hours under reduced pressure of 15 mm Hg. Thereafter a tube packed with 30 g of molecular sieve 3A was fitted on the reaction vessel so as to return the distilled solvent to the reaction vessel after passing through the molecular sieve layer and the reaction mixture was stirred at 130 °C for 30 hours under reduced pressure of 13 mm Hg.

[0090] The reaction mass obtained was dissolved in 720 ml of acetonitrile. The resulting solution was mixed with 300 ml of a 1N aqueous HCl solution, stirred for 0.5 hour, mixed with 320 ml of IPA and successively reprecipitated by pouring the mixture into 4.5 ℓ of methanol. The precipitate was washed with 3 ℓ of n-hexane and dried under reduced pressure. Polymer thus prepared had a weight average molecular weight of 137,000 and a residual tin catalyst content of 10 ppm or less.

35 Examples 2-1 to 2-5

[0091] Aliphatic polyesters obtained in Preparation Examples 1 to 5 were dried in a vacuum desiccator and melt-spun with a common extruder at 200 °C under extrusion pressure of 130 kg/cm² while ventilating nitrogen gas from a hopper. The extrudate was successively stretched 5 times at 80 °C and heat-set at 90 °C to obtain filaments of 500 deniers.

[0092] These filaments were plain-woven with a Rapier weaving machine so as to obtain a filament density of 24 filaments per inch in the longitudinal direction and 23 filaments per inch in a transverse direction. The fabrics obtained had a void volume of 60 %.

[0093] Following properties were measured on each fabric.

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(1) Tensile modulus and elongation at break :

[0094] The test was carried out in accordance with JIS L-1096. The fabrics were cut into rectangular forms and strengths in longitudinal and transverse directions were individually measured at a pulling rate of 200 mm/min.

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(2) Degradation in soil :

[0095] Fabrics having dimensions of 5× 5 cm were buried at 35 °C in soil having a moisture content of 30 %. Change in appearance was observed and loss in weight was measured. Results are illustrated in Table 1.

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Comparative Example 2-1

[0096] A fabric was prepared by carrying out the same procedures as described in Example 2-1 except that aliphatic

polyester was replaced by high density polyethylene. Properties of the fabric were measured by the same methods as above and results are illustrated in Table 1.

Comparative Example 2-2

[0097] A fabric was prepared by carrying out the same procedures as described in Example 2-1 except that aliphatic polyester was replaced by polylactic acid (L/DL = 50/50 wt%) having a weight average molecular weight of about 100,000. Properties of the fabric were measured by the same methods as above and results are illustrated in Table 1.

Examples 2-6 to 2-7

[0098] Polyester obtained in Preparation Example 1 was used. Fabrics were prepared by carrying out the same procedures as described in Example 2-1 except that size and density of the filament were changed. Properties of fabrics were measured by the same methods as above. Results are illustrated in Table 2.

Comparative Example 2-3

[0099] A fabric was prepared by carrying out the same procedures as described in Example 2-5 except that aliphatic polyester was replaced by polylactic acid (L/DL = 50/50 wt%) having a weight average molecular weight of about 100,000. Properties of the fabric were measured by the same methods as above and results are illustrated in Table 2.

Examples 4-1 to 4-5

[0100] Aliphatic polyesters obtained in preparation Examples 1 to 5 were dried in a vacuum desiccator and incorporated with 0.1 wt% of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole as an ultraviolet absorber and melt spun at 160 °C with a screw type small extruder. The filament thus obtained was cut into monofilaments of about 4 cm in length, stirred to form a random web and hot-pressed at 60 °C under pressure of 10 kg/cm² to obtain a degradable nonwoven fabric. The nonwoven fabric had a weight of 160 g /cm² and thickness of 2 mm.

[0101] The degradable nonwoven fabrics thus obtained had residual fibrous shape, hold cloth construction which clearly differs from a film made by melt process, and did not cause breakage or destruction of shape, even though both sides of the nonwoven fabrics were individually pinched with fingers and pulled respectively to the opposite direction.

[0102] Impact resilience, feeling and degradation in soil of these nonwoven fabrics were measured by the following methods.

① Impact resilience :

[0103] Measured in accordance with JIS K-6041.

[0104] A specimen having dimensions of 100 × 100 × 2 mm and parallel top- and under-surfaces was prepared. A steel ball of 5/8 regular grade specified in JIS B-1501 (ball for ball bearing) was made a free falling without rotation from a distance 460 mm above the top surface of the specimen, and the maximum rebound distance was measured. Impact resilience was calculated by the formula :

$$R = D_1 \times D_0 \times 100$$

wherein

R is rebound resilience (%),
D₀ is falling distance 460 (mm), and
D₁ is rebound distance (mm).

② Feeling :

[0105] Nonwoven fabrics obtained were brought into contact with a hand and the touch was classified into the following four groups.

Standard 1 : The touch is stiff.

- 2 : The touch is somewhat stiff.
3 : The touch is somewhat soft.
4 : The touch is soft.

5 ③ Degradation in soil :

[0106] A nonwoven fabric having dimensions of 50 × 50 mm was buried at 35 °C in soil having a moisture content of 30 %. After 2 months, change in appearance of the nonwoven fabric was observed.

[0107] These results are summarized in Table 3.

10 Comparative Example 4-1

15 [0108] A nonwoven fabric was prepared by carrying out the same procedures as described in Example 4-1 except that the aliphatic polyester was replaced by high density polyethylene having density of 0.95 g/cm³ and a melt index MI of 1.0 g/10 min, and spinning was conducted at 200 °C. Properties of the nonwoven fabric were measured by the same methods as above and results are illustrated in Table 3.

Comparative Example 4-2

20 [0109] A nonwoven fabric was prepared by carrying out the same procedures as described in Example 4-1 except that the aliphatic polyester was replaced by poly-L-lactic acid having an average molecular weight of about 110,000, and spinning was conducted at 180 °C. Properties of the nonwoven fabric were measured by the same methods as above and results are illustrated in Table 3.

25 [0110] However, these examples are not intended to limit of the scope of the present invention. This may be practiced or embodied in still other ways without departing from the spirit or essential character thereof.

Table 1

	Example 2-1	Example 2-2	Example 2-3	Example 2-4	Example 2-5	Comparative Example 2-1	Comparative Example 2-2
Polymer	P-1	P-2	P-3	P-4	P-5	polyethylene	polylactic acid
Filament size (denier)	500	500	500	500	500	500	500
Filament density (void volume %)	60	60	60	60	60	60	60
Tensile modulus (kgf/cm ²) longitudinal direction transverse direction	6100 5700	6400 6100	7000 6800	5300 5100	5200 5000	10,000 9,600	28,000 26,000
Elongation at break (%) longitudinal direction transverse direction	33 33	30 31	28 29	26 27	27 28	28 28	21 23
Degradation in soil (2 month) appearance	fabric was destructed by weak force						fabric was destructed by weak force
weight loss (%)	31	29	30	25	29	0	22

Table 2

	Example 2-6	Example 2-7	Comparative Example 2-3
Polymer	P-1	P-2	polylactic acid
Filament size (denier)	250	1000	1000
Filament density (void volume %)	70	60	60
Tensile modulus (kgf/cm ²) longitudinal direction transverse direction	5800 5500	6300 6100	30,000 28,000
Elongation at break (%) longitudinal direction transverse direction	27 28	35 34	25 27
Degradation in soil (2 months) appearance	fabric was destructed by weak force		
weight loss (%)	34	31	20

Table 3

	Example 4-1	Example 4-2	Example 4-3	Example 4-4	Example 4-5	Comparative Example 4-1	Comparative Example 4-2
Polymer	P-1	P-2	P-3	P-4	P-5	polyethylene	polylactic acid
Impact resilience (%)	15	14	14	15	15	13	7
Feeling	4	4	3	3	4	4	1
Degradation in soil (2 month) Appearance	fabric was destructed by weak force					no change	fabric was destructed by weak force

Claims

1. A degradable thermoplastic polymer formed product comprising an aliphatic polyester having a molecular weight of 50,000 or more which is obtainable by the polycondensation reaction of an aliphatic polyhydric alcohol or a mixture thereof with an aliphatic polybasic acid or a mixture thereof, or additionally a hydroxycarboxylic acid or a mixture thereof, or an oligomer resulting from these raw materials, in a reaction mixture comprising an organic solvent, wherein the formed product is a fabric or a non-moven fabric, with the proviso that the fabric is no net.
2. The degradable thermoplastic polymer formed product of claim 1 wherein the aliphatic polybasic acid is succinic acid.
3. The degradable thermoplastic polymer formed product of claim 1 or claim 2 wherein the aliphatic polyhydric alcohol is ethylene glycol or 1,4-butanediol.
4. The degradable thermoplastic polymer formed product of any of claims 1 to 3 wherein the polycondensation reaction is conducted in the presence of a catalyst.
5. The degradable thermoplastic polymer formed product of claim 4 wherein the catalyst content in the aliphatic polyester is 50 ppm or less.

Patentansprüche

1. Gegenstand aus abbaubarem thermoplastischen Polymer, enthaltend einen aliphatischen Polyester mit einem Molekulargewicht von 50 000 oder mehr, der durch die Polykondensationsreaktion eines aliphatischen mehrwertigen Alkohols oder eines Gemisches davon mit einer aliphatischen mehrbasigen Säure oder einem Gemisch davon oder zusätzlich einer Hydroxycarbonsäure oder einem Gemisch davon oder einem Oligomer, das aus diesen Ausgangsmaterialien erhalten wird, in einem Reaktionsgemisch, welches ein organisches Lösungsmittel enthält, wobei der Gegenstand ein Gewebe oder ein Vliesstoff ist, mit der Maßgabe, daß das Gewebe kein Netz ist.
2. Abbaubarer Gegenstand aus thermoplastischem Polymer nach Anspruch 1, worin die aliphatische mehrbasige Säure Bernsteinsäure ist.
3. Abbaubarer Gegenstand aus thermoplastischem Polymer nach Anspruch 1 oder 2, worin der aliphatische mehrwertige Alkohol Ethylenglycol oder 1,4-Butandiol ist.
4. Abbaubarer Gegenstand aus thermoplastischem Polymer nach einem der Ansprüche 1 bis 3, wobei die Polykondensationsreaktion in Anwesenheit eines Katalysators durchgeführt wird.
5. Abbaubarer Gegenstand aus thermoplastischem Polymer nach Anspruch 4, worin der Katalysatorgehalt in dem aliphatischen Polyester 50 ppm oder weniger ist.

Revendications

1. Produit obtenu par formage d'un polymère thermoplastique dégradable, comprenant un polyester aliphatique ayant une masse molaire d'au moins 50 000 et pouvant être obtenu par la réaction de polycondensation d'un polyalcool aliphatique ou d'un mélange de tels polyalcools avec un polyacide aliphatique ou un mélange de tels polyacides, plus éventuellement un acide hydroxycarboxylique ou un mélange de tels acides, ou un oligomère obtenu à partir de ces produits de départ, dans un mélange réactionnel contenant un solvant organique, le produit obtenu par formage étant un tissu ou un non-tissé, à condition que le tissu ne soit pas un filet.
2. Produit obtenu par formage d'un polymère thermoplastique dégradable selon la revendication 1, dans lequel le polyacide aliphatique est l'acide succinique.
3. Produit obtenu par formage d'un polymère thermoplastique dégradable selon la revendication 1 ou 2, dans lequel le polyalcool aliphatique est l'éthylèneglycol ou le 1,4-butanediol.

4. Produit obtenu par formage d'un polymère thermoplastique dégradable selon l'une quelconque des revendications 1 à 3, dans lequel la réaction de polycondensation s'effectue en présence d'un catalyseur.
5. Produit obtenu par formage d'un polymère thermoplastique dégradable selon la revendication 4, dans lequel la teneur en catalyseur dans le polyester aliphatique est d'au plus 50 ppm.

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